DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the dispersing agent for emulsion polymerizations and aqueous emulsion which consist of denaturation polyvinyl alcohol. It is related with the aqueous emulsion which was excellent in both leaving stability the dispersing agent for emulsion polymerizations excellent in emulsion-polymerization stability, low temperature, and hot, and a water resisting property in more detail.
[0002]
[Description of the Prior Art]Conventionally polyvinyl alcohol (it may be hereafter written as PVA) An ethylenic unsaturated monomer, It is widely used as protective colloid for emulsion polymerizations of the vinyl ester system monomer represented by especially vinyl acetate, The vinyl ester system aqueous emulsion produced by carrying out an emulsion polymerization using this as protective colloid For papers, It is widely used in fields, such as the various binders the various adhesives the object for woodwork, for plastics, etc., the object for impregnated papers, for nonwoven products, etc., admixture, ****** material, a paint, paper coating, and textile processing. Such an aqueous emulsion by adjusting the saponification degree of a PVA system polymer, Generally viscosity was low, it had the viscosity near a Newtonian flow, and the object for prizes has been carried out to various uses from what has the temperature dependence of emulsion viscosity high viscosity generally and comparatively small being comparatively obtained from a waterproof good thing. However, the thing with this aqueous emulsion runs short of mobility (high-speed coating nature), and has a fault, like the rise of the emulsion viscosity at the time of low temperature with the large temperature dependence of emulsion viscosity with a bad water resisting property is remarkable.
It is known that the place where these character depends on the PVA system polymer used for the emulsion polymerization is size.

[0003]Namely, the PVA system polymer as a dispersing agent for emulsion polymerizations, Generally there are what is called the "full saponification PVA" of an about [saponification degree 98 mol %] and the "partial saponification PVA" of an about [saponification degree 88 mol %], When the former is used, there is a fault of a water resisting property and mobility (high-speed coating nature) having the comparatively remarkable rise of the emulsion viscosity at the time of low-temperature neglect of a good thing, and being easy to gel. On the other hand, when the latter PVA system polymer is used, the viscosity rise at the time of the low temperature of an emulsion and those for gelation properties have a fault inferior to the water resisting property of what is improved. In order to improve such a fault, concomitant use of both PVA system polymer, use of the PVA system polymer both interim saponification degree, etc. were performed, but a water resisting property and the low-temperature leaving stability of emulsion viscosity were not able to be satisfied simultaneously. Then, the vinyl alcohol system polymer containing an ethylene unit was proposed, and a water resisting property and low-temperature leaving stability have been improved substantially (JP,11-21529,A, JP,11-21380,A, JP,10-226774,A, etc.). However, from a viewpoint of emulsion-polymerization stability, even if it has an ethylene unit, although it is what is called the full saponification PVA therefore, since it is inferior to the partial saponification PVA, the vinyl alcohol system polymer containing a lot of ethylene units must be

used as a dispersing agent. In order to use a lot of vinyl alcohol system polymers, the actual condition was that both a water resisting property and leaving stability are thoroughly unsatisfying.

[0004]

[Problem(s) to be Solved by the Invention]This invention is a basis of such a situation and an object of this invention is to provide the dispersing agent for emulsion polymerizations which can compound the aqueous emulsion which is excellent in emulsion-polymerization stability and is excellent in both a water resisting property and leaving stability.

[0005]

[Means for Solving the Problem]A result of having repeated research wholeheartedly this invention persons developing a dispersing agent for emulsion polymerizations which has the aforementioned desirable character, the alpha olefin unit X -- 1-20-mol % -- a dispersing agent for emulsion polymerizations which consists of a vinyl alcohol system polymer which contains, and as for which more than mol (1.7-X/40) % has a 1,2-glycol bond. And make this vinyl alcohol system polymer into a dispersing agent, and it finds out that it is that with which an aqueous emulsion which makes a dispersoid a polymer which has a kind or two sorts or more of unsaturation monomeric units chosen from an ethylenic unsaturated monomer and a diene system monomer is satisfied of the above-mentioned purpose, It came to complete this invention.

[0006]

[Embodiment of the Invention]the alpha olefin unit X used for the dispersing agent for emulsion polymerizations of this invention -- 1-20-mol % -- it contains, there is no restriction in particular as a manufacturing method of the vinyl alcohol system polymer as for which more than mol (1.7-X/40) % has a 1,2-glycol bond, and it is usable in a publicly known method. How to carry out copolymerization of the vinylene carbonate to ethylene and a vinyl ester system monomer as an example, so that it may become the above-mentioned amount of 1,2-glycol bonds, When carrying out copolymerization of the vinyl ester system monomer to ethylene, the method of polymerizing under application of pressure, etc. are mentioned in polymerization temperature at a temperature higher than the usual conditions, for example, 75-200 **. In the latter method, as for polymerization temperature, it is preferred that it is 90-190 **, and it is preferred that it is especially 100-180 **.

[0007]As for the content of 1 and 2-glycol bond, more than mol % is [more than mol (1.75-X/40) %] more than mol (1.9-X/40) % the optimal further (1.8-X/40) more preferably [it is required to be more than mol (1.7-X/40) %, and]. It is desirable still more preferred that it is less than 4 mol %, and the content of 1 and 2-glycol bond is less than 3.2 mol % at a 3.5 mol % less or equal and optimum. The content of 1 and 2-glycol bond is calculated from the analysis of an NMR spectrum here. It is important that it is [1-20 mol] %, the content of an alpha olefin unit is more than 1.5 mol % and also more than 2 mol % more preferably, and less than 19 mol % and also less than 15 mol % are preferred for it.

[0008]Here, although formic acid vinyl, vinyl acetate, vinyl propionate, vinyl pivalate, etc. are mentioned as a vinyl ester system monomer, generally vinyl acetate is used preferably. Especially ethylene is preferred although with a carbon numbers [, such as ethylene, propylene, butylene, and isobutylene,] of four or less alpha olefin is mentioned as a suitable thing as alpha olefin.

[0009]What carried out copolymerization of the copolymerizable ethylenic unsaturated monomer in the range which does not spoil the effect of this invention may be sufficient as this vinyl alcohol system polymer. As such an ethylenic unsaturated monomer, For example, acrylic acid, methacrylic acid, fumaric acid, maleic acid (anhydrous), (Anhydrous) Itaconic acid, acrylonitrile, a methacrylonitrile,

acrylamide, Methacrylamide, trimethyl (3-acrylamide 3-dimethylpropyl)-ammonium chloride, Acrylamide 2-methylpropanesulfonic acid and its sodium salt, Ethyl vinyl ether, butylvinyl ether, N-vinyl pyrrolidone, VCM/PVC, vinyl bromide, and vinyl fluoridation, a vinylidene chloride, vinylidene fluoride, N-vinylamide, such as tetrafluoroethylene, sodium vinylsulfonate, sodium allylsulfonate, N-vinyl pyrrolidone, N-vinylformamide, and N-vinylacetamide, is mentioned. Under existence of thiol compounds, such as thiol acetic acid and mercaptopropionic acid, copolymerization of the vinyl ester system monomers, such as vinyl acetate, can be carried out to ethylene, and the terminal modification thing obtained by saponifying it can also be used.

[0010]although the saponification degree in particular of the vinyl alcohol system polymer used for the dispersing agent for emulsion polymerizations of this invention is not restricted, the thing beyond 60 mol % is usually used -- more -- desirable -- more than 70 mol % -- it is more than 75 mol % still more preferably. When a saponification degree is less than [60 mol %], the concern to which the water solubility which is the original character of a vinyl alcohol system polymer falls arises. Although the degree of polymerization in particular of this vinyl alcohol system polymer is not restricted, either, the thing of the range of 100-8000 is usually used, and 300-3000 are used more preferably. When a degree of polymerization is less than 100, and a vinyl alcohol system polymer is used as a dispersing agent, and the feature as protective colloid is not demonstrated but it exceeds 8000, there is a problem in industrial manufacture of this vinyl alcohol system polymer.

[0011]The dispersing agent for emulsion polymerizations of this invention is useful as a dispersing agent for emulsion polymerizations of a kind chosen from an ethylenic unsaturated monomer and a diene system monomer, or two sorts or more of unsaturated monomers. As an unsaturated monomer which constitutes the dispersoid of an aqueous emulsion here, Olefins, such as ethylene, propylene, and isobutylene, VCM/PVC, Halogenation olefins, such as vinyl fluoridation, vinylidenechloride, and a vinylidenefluoride, Vinyl ester, such as formic acid vinyl, vinyl acetate, vinyl propionate, and BASA tic acid vinyl, Acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, Butyl acrylate, 2-ethylhexyl acrylate, acrylic acid dodecyl, Acrylic ester, such as acrylic acid 2-hydroxyethyl, methyl methacrylate, Ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, Methacrylic acid ester, such as methacrylic acid dodecyl and methacrylic acid 2-hydroxyethyl, To acrylic acid dimethylaminoethyl, dimethylaminoethyl methacrylate and the fourth class ghosts of these, and a pan. Acrylamide system monomers, such as acrylamide, methacrylamide, N-methylolacrylamide, N,N-dimethylacrylamide, and acrylamide 2-methylpropanesulfonic acid and its sodium salt, styrene, alpha-methylstyrene, Diene system monomers, such as butadiene, such as styrene monomers, such as p-styrene sulfonic acid and sodium, and potassium salt, and other N-vinyl pyrrolidone, isoprene, and chloroprene, are mentioned, independent, two or more sorts are mixed, and these are used.

[0012]Also in the above-mentioned ethylenic unsaturated monomer, concomitant use with a vinyl ester system monomer, and ethylene and a vinyl ester system monomer is preferred. As a vinyl ester system monomer, although formic acid vinyl, vinyl acetate, vinyl propionate, vinyl pivalate, etc. are mentioned, vinyl acetate is preferred.

[0013]When using the dispersing agent for emulsion polymerizations of this invention, there is no restriction in particular about the amount of the dispersing agent used, but it is the range of four to 13 weight section more preferably three to 15 weight section one to 20 weight section to unsaturated monomer 100 weight section. When the amount of this [used] is less than one weight section, there is a possibility that emulsion-polymerization stability may fall, and when exceeding 20 weight sections, the

leaving stability of the obtained emulsion may fall. Furthermore, in this invention, even if the amount of the vinyl alcohol system polymer used used as a dispersing agent is little, it can attain the purpose of this invention enough.

[0014]The dispersing agent for emulsion polymerizations of this invention is a range which does not spoil the effect of this invention, and use of other protective colloid or an emulsifier is also possible for it. For example, the conventional PVA, starch, polyacrylamide, hydroxyethyl cellulose, anionic [conventionally publicly known], and a nonionic or cationic surface-active agent can be used together.

[0015]The aqueous emulsion which the dispersing agent for emulsion polymerizations of this invention excels [aqueous emulsion] in emulsion-polymerization stability, and is obtained using the dispersing agent for these emulsion polymerizations is excellent in a water resisting property and leaving stability.

[0016]

[Example]Next, an example and a comparative example explain this invention still in detail. A weight reference is meant unless it refuses especially a "part" and"%" in the following examples and comparative examples. The following way estimated the water resisting property of the obtained emulsion, and leaving stability.

[0017](Evaluation of an emulsion)

(1) Water resistant adhesion (adhesion of a tree)

150 g/m2 of obtained aqueous emulsions were applied to the hemlock fir (straight wood grain), were pasted together, and it pressed by 7 kg/m2 of load for 16 hours. Then, after decompressing and recuperating oneself for five days under 20 ** and 65%RH, it was immersed in 20 ** chilled water for four days, and the compression shear strength was measured in the state where it has wetted wet.

(2) Water resistant adhesion (adhesion of paper)

30 g/m2 of obtained aqueous emulsions were applied to kraft, were pasted together, and it pressed 3 times with the hand roll. The obtained processed goods were immersed in underwater [20 **] after desiccation for 24 hours, and the subsequent adhesion state was observed. O Viscosity change 100 days after [at the time of neglecting paper breaking and a x exfoliation (3) leaving-stability examination emulsion at 0 ** and 60 ** paper breaking and a little / **] was observed.

[0018]Example of manufacture 1 agitator, a nitrogen feed port, and an initiator feed port to 5L application-of-pressure reaction vessel which it had 2850 g of vinyl acetate, After carrying out pressure up of the reaction-vessel pressure and neglecting it for 10 minutes to 2.0MPa, having prepared the methanol 150g and the tartaric acid 0.086g, and carrying out bubbling by nitrogen gas under a room temperature, operation of discharging pressure was repeated 3 times and the nitrogen purge of the inside of a system was carried out. The concentration solution of 0.1 g/L which dissolved 2,2'-azobis (N-butyl-2-methylpropionamide) in methanol as an initiator was prepared, and the nitrogen purge of the bubbling by nitrogen gas was performed and carried out. Subsequently, temperature up of the above-mentioned polymerization tank internal temperature was carried out to 150 **, ethylene was introduced, and the reaction-vessel pressure was set to 20MPa. Subsequently, 15.0 ml of the above-mentioned initiator solutions were poured in, and the polymerization was started. During the polymerization, polymerization temperature was maintained at 150 ** and it polymerized by carrying out continuation addition of the 2,2'-azobis (N-butyl-2-methylpropionamide) by 15.8 ml/hr using the above-mentioned initiator solution. The reaction-vessel pressures under polymerization were 20MPa. It cooled 4 hours afterward and the polymerization was suspended. The solids concentration at this time was 35%. Subsequently, the unreacted vinyl acetate monomer was removed sometimes adding methanol under 30 ** decompression,

and the methanol solution (33% of concentration) of polyvinyl acetate was obtained. To the methanol solution 400g (100g of polyvinyl acetate in a solution) of polyvinyl acetate adjusted so that methanol might be added to this obtained polyvinyl acetate solution and concentration might be 25%. It saponified at 40 ** by adding a 11.6 g (it is the mole ratio (MR) 0.025 to the vinyl acetate unit in polyvinyl acetate) alkali solution (10% methanol solution of NaOH). The crusher ground what was gelled in about 3 minutes after alkali addition, and after neglecting it for 1 hour and advancing saponification, the alkali which adds 1000 g of methyl acetate and remains was neutralized. The methanol 1000g was added to PVA of the white solid produced by filtering after checking the end of neutralization using the phenolphthalein indicator, and neglect washing was carried out at the room temperature for 3 hours. After repeating the above-mentioned washing operation 3 times, PVA produced by carrying out centrifugal deliquoring was neglected for two days at 70 ** among the dryer, and the desiccation PVA (PVA-1) was obtained. The saponification degree of obtained PVA (PVA-1) was 98-mol %. After saponifying the methanol solution of the polyvinyl acetate produced by removing an after-polymerization unreacted vinyl acetate monomer by the alkali mole ratio 0.5, After neglecting at 60 ** what was ground for 5 hours and advancing saponification, Soxhlet washing by methanol was carried out for three days, subsequently reduced pressure drying was performed for three days at 80 **, and the refining PVA was obtained. It was 1000 when the average degree of polymerization of this PVA was measured according to JIS K6726 of a conventional method. When 1 of this refining PVA and the amount of 2-glycol bonds were calculated from measurement by a 500-MHz proton NMR (JEOL GX-500) device as above-mentioned, it was 2.5-mol %. The content of the ethylene unit was 4-mol %.

[0019]PVA-2 and PVA-3 were obtained by the same method as the example 2 of manufacture - the example 1 of 3 manufactures. As for the average degree of polymerization of PVA-2 (polymerization temperature: 90 **), the content of the ethylene unit of the amount of 1 and 2-glycol bonds was 4-mol % 1.8-mol% 2100 and saponification degree% of 97.7 mol. As for the average degree of polymerization of PVA-3 (polymerization temperature: 150 **), the content of the ethylene unit of the amount of 1 and 2-glycol bonds was 4-mol % 2.4-mol% 450 and saponification degree% of 98.5 mol.

[0020]To example 1 reflux condenser, a dropping funnel, a thermometer, and the 1-l. glass polymerization vessels provided with the nitrogen blowing-in mouth. PVA-1(degree-of-polymerization 1000 and saponification degree % of 98 mol, and 1 and 2-glycol content % and ethylene-unit-content [of 4 mol] % of 2.5 mol)26g obtained by the ion exchange water 300 and the example 1 of manufacture was taught, and it dissolved thoroughly at 95 **. Next, after carrying out temperature up to 60 **, agitating this PVA solution at 200 rpm after cooling and a nitrogen purge, 4.4g and the 5% hydrogen peroxide solution 3g (it is 0.015 at a mole ratio to vinyl acetate) were prepared [the 10% solution of tartaric acid] after shot addition and for 26 g of vinyl acetate, and the polymerization was started. The end of an initial polymerization was checked 30 minutes after the polymerization start. It went over 0.9g and the 5% hydrogen peroxide solution 3g after shot addition, went over 234 g of vinyl acetate in 2 hours, the 10% solution of tartaric acid was added continuously, and the polymerization was completed. It filtered after cooling using the wire gauze made from stainless steel of 60 meshes. The filtration residue after filtration estimated polymerization stability on the following standard.

O Polymerization stability is excellent, so that there are few 0.5-2g x ******-less O less than 0.5 g ** 2 or more g filtration residues, and it is shown that polymerization stability is so bad that it is large. As for the above result, the polyvinyl acetate system emulsion of 47.3% of solids concentration was obtained. Addition mixing of five copies of dibutyl phthalates was carried out to 100 weight sections of this

emulsion (Em-1). The above-mentioned method estimated this emulsion. A result is shown in Table 1.
[0021]PVA-4 manufactured by the conventional method instead of using PVA-1 used in comparative example 1 Example 1 (PVA-110 by Kuraray Co., Ltd.; the degree of polymerization 1000 and 98.0% of a saponification degree) 1 and 2-glycol content % of 1.6 mol was used, and also (Em-2) of 47.1% of solids concentration was obtained like Example 1. The above-mentioned method estimated this emulsion. In accordance with a result, it is shown in Table 1.
[0022]To example 2 reflux condenser, a dropping funnel, a thermometer, and the 1-l. glass polymerization vessels provided with the nitrogen blowing-in mouth. PVA-2 (degree-of-polymerization 2100 and saponification degree % of 97.7 mol, and 1 and 2-glycol content % and ethylene-unit-content [of 4 mol] % of 1.8 mol) 13g obtained by the ion exchange water 300 and the example 2 of manufacture was taught, and it dissolved thoroughly at 95 **. Next, after carrying out temperature up to 60 **, agitating this PVA solution at 200 rpm after cooling and a nitrogen purge, the 10% solution 18g and 26 g of vinyl acetate of tartaric acid were taught, the hydrogen peroxide solution 85g was continuously added over 2.5 hours 1%, and the polymerization was started. The end of an initial polymerization was checked 30 minutes after the polymerization start, and 234 g of vinyl acetate was further added continuously over 2 hours. The hydrogen peroxide solution 4.8g was added at the shot 1% after the end of vinyl acetate addition, and the polymerization was completed. It filtered after cooling using the wire gauze made from stainless steel of 60 meshes. With the filtration residue after filtration, the same method as Example 1 estimated polymerization stability. As for the above result, the polyvinyl acetate system emulsion of 47.6% of solids concentration was obtained. Addition mixing of five copies of dibutyl phthalates was carried out to emulsion 100 weight section furthermore obtained (Em-3). The above-mentioned method estimated this emulsion. In accordance with a result, it is shown in Table 1.
[0023]PVA-5 (degree-of-polymerization 2000 and saponification degree % of 98.5 mol.) manufactured by the conventional method instead of using PVA-2 used in comparative example 2 Example 2 1 and 2-glycol content % of 1.6 mol was used, and also (Em-4) of 47.4% of solids concentration was obtained like Example 2. The above-mentioned method estimated this emulsion. In accordance with a result, it is shown in Table 1.
[0024]PVA-3 (degree-of-polymerization 450 and saponification degree % of 98.5 mol.) obtained by the example 3 of manufacture instead of using PVA-1 used in example 3 Example 1 1 and 2-glycol content % and ethylene-unit-content [of 4 mol] % of 2.4 mol was used, and also (Em-5) of 47.7% of solids concentration was obtained like Example 1. The above-mentioned method estimated this emulsion. In accordance with a result, it is shown in Table 1.
[0025]PVA-6 (Kuraray Co., Ltd. make PVA-105; degree-of-polymerization 500 and saponification degree [of 98.5 mol] %.) manufactured by the conventional method instead of using PVA-1 used in comparative example 3 Example 1 1 and 2-glycol content % of 1.6 mol was used, and also (Em-6) of 47.6% of solids concentration was obtained like Example 1. The above-mentioned method estimated this emulsion. In accordance with a result, it is shown in Table 1.
[0026]
[Table 1]

	PVA	エマルジョン	重合安定性	耐水性		放置安定性	
				紙の接着	木の接着(kg/cm^2)	0℃	60℃
実施例1	PVA-1	Em-1	○	○	10	変化なし	変化なし
比較例1	PVA-4	Em-2	△	△	6	1.2倍に増粘	変化なし
実施例2	PVA-2	Em-3	◎	○	15	1.5倍に増粘	変化なし
比較例2	PVA-5	Em-4	△	△	7	ゲル化	変化なし
実施例3	PVA-3	Em-5	○	○	8	変化なし	変化なし
比較例3	PVA-6	Em-6	×	×	0	1.2倍に増粘	変化なし

[0027]PVA-1; 2.5 mol of degree-of-polymerization 1000 and saponification degree % of 98 mol, and 1 and 2-glycol bond content %, Ethylene-unit-content 4 mol %PVA-2; Degree-of-polymerization 2100 and saponification degree % of 97.7 mol, 1.8 mol of 1 and 2-glycol bond content %, ethylene-unit-content 4 mol % PVA-3; Degree-of-polymerization 450 and saponification degree % of 98.5 mol, 2.4 mol of 1 and 2-glycol bond content %, ethylene-unit-content 4 mol %PVA-4; 1.6 mol of degree-of-polymerization 1000 and saponification degree % of 98.0 mol, and 1 and 2-glycol bond content % {PVA-110 by Kuraray Co., Ltd.} PVA-5; degree-of-polymerization 2000 and saponification degree [of 98.5 mol] %, 1, 2-glycol bond content 1.6 mol %PVA-6; 1.6 mol of degree-of-polymerization 500 and saponification degree % of 98.5 mol, and 1 and 2-glycol bond content % {PVA-105 by Kuraray Co., Ltd.}

[0028]

[Effect of the Invention]Since it excels in a water resisting property and leaving stability, the aqueous emulsion which the dispersing agent for emulsion polymerizations of this invention excelled [aqueous emulsion] in the emulsion-polymerization stability of the vinyl compound, and was obtained using this dispersing agent for emulsion polymerizations is used suitably for various uses.

[Translation done.]